

MINIMIZING CORROSION AND BUILD-UP IN A
FLUE-GAS SYSTEM INCLUDING A DESULFURIZER

The present invention minimizes corrosion and build-up in a flue-gas system including a desulfurizer and heat transfer means communicating with the desulfurizer where significant amounts of moisture and/or sulfuric acid are present by adding to the flue-gas while it is at a relatively high temperature a readily water soluble alkaline substance such as sodium hydroxide in an amount sufficient to produce with said flue-gases as they leave the heat transfer means a pH of a minimum of about 5, preferably 7 or higher.

BACKGROUND OF THE INVENTION

In most flue-gas systems, for safety and environmental reasons, as a means of conserving heat, the flue-gas leaving the furnace at relatively high temperatures is passed through a variety of treatment devices before escaping into the atmosphere. Among these devices are, usually in sequence, a boiler or heater, a precipitator, a heat transfer device such as a gas/gas heater, and a scrubber or desulfurizer, the flue-gas then returning to the gas/gas heater on its way to the stack. The temperature of the flue-gas decreases as the gas passes through the system, and in the course of that temperature decrease moisture, originally in the form of steam, and even containing sulfuric acid, comes into being as a liquid which deposits on the surfaces of the system, and particularly on the gas/gas heater surfaces, the sulfuric acid

content of that liquid producing corrosion and the solid content of the flue-gas tending to deposit and build-up on exposed system surfaces.

It has long been customary to add substances to the flue-gas to minimize or prevent corrosion of the exposed surfaces of the system. (My prior patents, No. 4,842,617 of June 27, 1989 entitled "Combustion Control By Addition of Magnesium Compounds of Particular Particle Sizes", and No. 5,034,114 of July 23, 1991 entitled "Acid Neutralizing Composition Additive With Detergent Builder" are representative of the use of such additives, as is a pending application Serial No. 814,598 of March 23, 2001 entitled "Use Of Expanded Agents For Minimizing Corrosion And Build-Up Of Deposits In Flue-Gas Systems", the invention of myself and William Carmen Pepe.) The corrosive action of sulfuric acid on exposed surfaces of the system is obviously undesirable and it is therefore common to add such substances as limestone or magnesium oxide to the system to neutralize the sulfuric acid. Because a solid/liquid reaction rate is generally slow, relatively large amounts of such additives must be provided. They are usually pneumatically injected into the affected portion of the system through conduits, usually in the form of pipes, using pressurized air as the vehicle to transport the additives through the conduit to the injection location in the system. The act of compressing air generates both heat and moisture, and hence the pressurized air which does the conveying is usually both moisture-laden and hot. Movement of the pressurized additive through the conduits results in some condensa-

tion of the moisture on the conduit surface and this enhances the tendency of the solid additives to stick to and build-up on those surfaces. As a result it is periodically necessary to take the injection equipment off line for cleaning, a process which is itself costly and time consuming, and while the injection equipment is off line no anti-corrosion additive is fed to the system, thus increasing the likelihood of corrosion.

When the system is provided with a scrubber or desulfurizer the flue-gas emanating from the scrubber has a comparatively high moisture content and a comparatively low temperature, thus leading to the condensation of comparatively large volumes of moisture, significantly including sulfuric acid in its liquid form because its temperature is below its dew point. When, as is usually the case, the output from the scrubber is fed back to the gas/gas heater the moisture content of the flue-gas becomes a significant corrosion-producing factor.

Previous attempts to solve this problem, as for example the injection of lime, limestone, magnesium oxide, magnesium hydroxide, or other basifying agents that are insoluble in water, have two major drawbacks. Because these products are insoluble in water, they are most unreactive or very slowly reactive, particularly where the neutralization of the acidity takes place in the steam which exists because of the high temperatures involved, and as a result excess amounts of basifying agent relative to the amount of SO_3 that has to be neutralized are required, and the use of such a large excess of these inefficient basifying agents results in

clogging and deposit build-up on the gas/gas heater inlet plates, rendering the gas/gas heaters inoperative.

SUMMARY OF THE INVENTION

We have discovered that corrosion of the system surfaces, and particularly the inlet surfaces of a scrubber and gas/gas heater used in conjunction therewith, can be significantly reduced, and the build-up on those surfaces of residue particularly from the substances described above, which have been added to the system for various purposes, can likewise be significantly reduced or even substantially eliminated, by not using such substances at all, but rather by applying to the flue-gas, while it is in the heat transfer means upstream of said scrubber, where its temperature is well above the boiling point of water, an alkaline substance which is readily water-soluble in an amount sufficient to bring the flue-gas-additive combination as it leaves the heat transfer means to a minimum pH 5, preferably 7 or higher. In particular, the alkaline material, preferably in the form of a water solution, is added to the flue-gas while the moisture content of the flue-gas is in the form of steam. Significantly, the amount of such alkaline substance which must be added is in general that amount required to neutralize the acid content of the flue-gas. This in itself is a significant factor, since the prior art additives, generally insoluble or difficultly soluble, must be added in amounts substantially greater than the stoichiometric amounts in order to obtain the desired neutralization but by the same token increasing

the build-up which is so undesirable. With the use of this invention the SO_3 acid dew point of the vapor stream from the heat transfer means is reduced from above 300°F. to 250°F. or even lower which minimizes condensation of sulfuric acid in the gas/gas heaters, even at the high humidities present at the heater plates. The actual untreated SO_3 dew point is dependent upon the amount of SO_3 present in the flue-gases. A dew point of 300°F. represents a concentration of 61 parts per million of sulfuric acid while an acid dew point of 250°F. represents a concentration of only 2 parts per million.

The amount of basifying agent required can be determined by measuring the acid dew point of the gases in or leaving the gas/gas heater, which can be done manually, or preferably with a continuous, on-line, automatic acid dew point meter, and the using of the latter to regulate the feed rate of the aqueous basifying agent.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 discloses diagrammatically a typical flue-gas system in which the method of the present invention is particularly useful.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A typical flue-gas system such as is shown in Fig. 1 comprises a furnace or boiler 2 where steam is generated. Ambient air enters the system at 4 and passes through a primary air heater 6 in which it is heated to perhaps 150°F. and it then enters the furnace 2 to combine with fuel for combustion purposes. A waste product from

the combustion in the furnace 2 is the flue-gas which exits the furnace at 8 at a temperature of perhaps 800° F. The flue-gas passes through the air heater 6, providing the means for the initial heating of the ambient air, and the flue-gas which leaves the air heater 6, at 10, will have lost a great deal of its heat and be at a temperature of about 350° F. to 400° F. It then passes into an electrostatic precipitator 12 in which certain impurities are removed, and it escapes from the precipitator 12 at 14 at a further reduced temperature of about 275° to 300° F. Because of its reduced temperature the flue-gas may now have a significant moisture content of perhaps 5-15%. The flue-gas goes into the upper portion 16A of a heat transfer means, here shown as a gas/gas heater 16, from which it escapes to point 18 at a temperature of less than 250° F. and it then passes through a desulfurizer or scrubber 20 which it leaves at point 22 at a temperature of perhaps 100° F.-150° F. and with a moisture content of perhaps 40-50%. The gas is then fed back through the lower portion 16B of the gas/gas heater 16 and escapes through the stack at 24.

The gas/gas heater 16 has structural parts which move from the upper hot portion of 16A to the lower or relatively cool portion of 16B and back again. It will be apparent that exposed surfaces of the gas/gas heater 16, and particularly those surfaces thereof which at any given moment are in the lower portion 16B of the heater, are very susceptible to acid corrosion because of the high moisture content and low temperatures to which they are subjected, so that the metal temperature is below the acid dew point. From

the point of view of minimizing corrosion in the gas/gas heater 16 it is at the area 14 immediately up-stream of the gas/gas heater 16 where the usual corrosion-minimizing additives are injected into the system, as indicated by the arrow 26.

The susceptibility of the gas/gas heater 16 to corrosion can perhaps be best appreciated by considering that scrubber 20 more easily and effectively absorbs impurities from the flue-gas when the flue-gas is at or below its dew point, and when the flue-gas exits the scrubber 20 its temperature is below the dew point to an even greater degree, thereby increasing its moisture content and making corrosion more likely. Also, because structural parts of the gas/gas heater 16 move sequentially through the upper and lower portions 16A and 16B thereof, they are constantly subjected to variations in temperature, and the constant heating and cooling of the structural parts of the gas/gas heater 16, coupled with the resultant high moisture content of the flue-gas as that passes through the heater, produces a situation ideal for corrosion and for deposit build-up.

Also, with the previous usage of lime, limestone or magnesium, additive builds up in the conduit feeding those additives to the system. The additives are preferably injected into the system between the precipitator 12 and the gas/gas heater 16, as indicated by the arrow 26, so that they can perform their desired action where that action is most needed, to wit, in the gas/gas heater 16.

The conventional, previously used, anti-corrosion additives, such as calcium oxide, calcium hydroxide, calcium carbonate,

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dolomite, dolomitic lime, lime, calcium hydrate, limestone, magnesium oxide, magnesium hydroxide, magnesium carbonate, as well as combinations thereof such as calcium/magnesium oxides and hydroxides, are relatively ineffective because of the relative slowness of the reaction between these basifying additives and the sulfur trioxide that they are designed to neutralize, and those additives must be provided in relatively large quantities, well in excess of the stoichiometric amount required to neutralize the acidic constituents. As a result the problem involved in preventing build-up in the conduits through which those basifying agents are fed is intensified, and the inevitable deposit build-up on the gas/gas heaters results in a rapid shut down of the scrubber.

According to the present invention the build-up problem, both in the additive conduit and on the perforated gas/gas heater revolving plates, is eliminated and the corrosion problem, particularly in the gas/gas heater 16, is minimized or virtually eliminated with the use of the water-soluble basifying agents described herein added to the system as shown.

In the embodiment of the present invention here specifically disclosed the system comprises a desulfurizer or scrubber 20 functioning in combination with a heat transfer means here specifically shown as a gas/gas heater 16. The upper portion 16A of the gas/gas heater 16 is at a higher temperature than its lower portion 16B. In particular, the temperature in the upper portion 16A is well above the boiling point of water. Hence the water content of the flue-gas is in the form of steam. It is when the

flue-gas enters the lower portion 16B of the gas/gas heater 16 that, because of the lower temperature in the region, the sulfuric acid content of the flue-gas is at or below its dew point, as a result of which corrosive sulfuric acid, if present, tends to form on the exposed surfaces of the gas/gas heater 16.

In accordance with the present invention, we take advantage of the high temperature of the flue-gas at the upper portion 16A of the gas/gas heater 16 to subject the flue-gas at that relatively high temperature to the action of a readily water soluble alkaline substance, preferably in the form of a water solution. Under those conditions the alkaline substance reacts substantially immediately and completely with the acid content of the flue-gas, neutralizing that acid content so that, when the flue-gas exits from the scrubber 20 and returns to the lower section 16B of the gas/gas heater 16 in a condition below its dew point, there will be little or no acid content available to produce corrosion. Thus by adding the alkaline substance in an area where, because of the high temperature, the liquid content from the flue-gas is in the form of vapor, the sought-for neutralization action is effectively achieved. Best results are obtained if the pH of the flue-gas after it leaves gas/gas heater 16 is at a minimum of 5, and preferably 7 or greater, and the optimum amount of alkaline substance added is that which produces the specified pH at that point in the system. This can, of course, be readily monitored by available sensors and control equipment.

Preferred alkaline substances for use in connection with the present invention are sodium hydroxide and sodium carbonate primarily because they are low cost materials, and the fact that the corrosion and build-up inhibition can be achieved with stoichiometric amounts of such low cost material is an exceedingly important advantage of the present invention. However, other substances having the same characteristics of alkalinity and ready water solubility could be employed. When certain chemicals often used in water treating systems are co-added with sodium hydroxide or sodium carbonate, this enhanced corrosion protection, and particularly helped to prevent clogging of the gas/gas heater openings even beyond that which was achieved with the use of either sodium hydroxide or sodium carbonate by itself. Particularly effective as co-additives were trisodium polyphosphate, trisodium phosphate, disodium monohydrogen phosphate, sodium borate, sodium di and polyborates, sodium silicates and sodium polysilicates, and in general water soluble sodium salts of the various phosphates, silicates and borates.

The effectiveness of the use of these basifying products having a high initial pH in minimizing corrosion or deposit build-up is shown by the following laboratory demonstration. In each of the following samples a mixture of 30 cc of water, 3 cc of 6 Normal sulfuric acid and 2 cc of the additive as described in Table I was observed after incubation at 130° C. for one hour with the results as set forth in Table I.

Table I

Basifying Agents to Prevent Corrosion of Gas/Gas Heaters
Connected to a Desulfurizer

<u>Sample No.</u>	<u>Composition of Additive</u>	<u>Results After Incubating at 130° for 1.5 Hours with Steel Metal Strip Exposed to Condensate from the Mixture of Dilute Sulfuric Acid and Additive</u>
1	No additive	Heavy corrosion, 1/8" of a deposited, brown, layer on bottom of metal specimen.
2	14 cc of 1.2 N caustic solution	No corrosion, very slight, scattered, brownish spots; trace of brown deposits on bottom 1/8" of metal specimen.
3	18 cc of 1.2N caustic solution	No corrosion; deposit-free metal specimen, trace spotting on bottom 1/8" of metal specimen.

Without the basifying additive, rapid corrosion of the steel metal strips takes place. In each case, the additive increased the pH of the solution from below 3 to over 8.

In another series of experiments as shown in Table II, use of combining basifying chemicals with deposit modifying, or anti-corrosion, enhancing chemicals show a further improvement when this combination is used.

Table II

Use of Combined Basifying Chemicals and Deposit-Modifying
or Anti-Corrosion, or
Enhancing Chemicals Are Used In Combination

<u>Sample No.</u>	<u>Composition of Additive</u>	<u>Results After Incubating at 130° for 1.5 Hours with Steel Metal Strip Exposed to Condensate from the Mixture of Dilute Sulfuric Acid and Additive</u>
1A	None	Metal completely covered with brown, rust-like, stain. Very heavy brownish/black coating on bottom 1/4" of metal specimen.
1B	18 cc of 1.2 N caustic solution	Essentially clear, very slight, scattered, brown spots, trace deposit on bottom 1/8" of metal specimen.
1C	15 cc of 1.2 N caustic solution, plus 0.70 cc of a 3% solution of trisodium phosphate	Totally clear, deposit-free, metal strip, no trace of deposit on bottom 1/8" of metal specimen.
1D	15 cc of 1.2 N caustic solution, plus 0.70 cc of a 3% solution of sodium tripolyphosphate	Totally clear, deposit-free, metal strip throughout.

The total amount of additives required is based on the flow rates of the flue-gas itself and the recirculating water solution from the scrubber 20, as well as the acidity present in the system. Basically, the feed rate of additive is determined primarily by the acidity of the stream and that amount of basifying agent, or basifying agent with modifier, that decrease the acid dew point of

the stream as it leaves the gas/gas heater 16 from plus 300° F. to 250° F. or less.

With a boiler of 200 megawatts, an SO₂ content of 6000 mg/Nm, and sulfuric acid content at the gas/gas heater of 30 ppm (112 mg/m³) and with a treatment rate of 600 ppm of a 5% solution of caustic, the following results were obtained. The acidity was reduced to 5.0 mg/Nm, or less than 2 ppm or 7.5 mg/m³. With the additive combination as shown in Example 1C of Table II, a treatment rate of 600 ppm reduced the acidity to 2.1 parts per million, or 7.8 mg/m³ without any corrosion or traces of deposits on the gas/gas heater plates.

The most cost effective treatment rates may vary from boiler to boiler and will depend upon the megawatts of the boiler, the temperature at the inlet and outlet of the gas/gas heater, the acidity of the return flow rate from the scrubber to the gas/gas heater, the design of the gas/gas heater and the amount of sulfur dioxide and sulfuric acid present and the amount of moisture in the condensate. Measurement of the acid dew point of the stream immediately prior to or after the gas/gas heater may be made by employing an on-line automatic acid dew point test apparatus, such as a Land Continuous Dewpoint Acid Monitor, which in turn can be connected to an automatic feed adjusting system that monitors the inlet feed rate of the aqueous basifying agents. The controlling feed rate is that amount of additive that increases the acid dew point of the circulating acid solution from the scrubber to below 250° F.

While but a single preferred embodiment is here specifically disclosed, it will be apparent that many variations may be made in the details of the method here disclosed, all within the scope of the instant invention as defined in the following claims.